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#1542

## On the Phototoxicity of Some Triazine Derivatives

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/TN: The following words are transliterations: propazin, ipazin, trietazine, khlorazin, atraton, and prometrin./

Herbicidal properties of symmetric triazines were studied intensively in 1958 -- 1960 [1 -- 3]. There were established several structural properties of the molecules which condition the activity and selectivity of triazine derivatives. Gysin and Knusli [3, 4] showed that compounds with a secondary aminoradical joined to the ring are more selective than compounds with a primary aminoradical. The most promising preparations for combatting weeds are the chlorine derivatives of triazine which have two atoms of carbon in the ring substituting for the ethylamino, isopropylamino, and allylamino and radicals. Compounds with alkoxy or alkylmercapto and radicals (especially metoxy or methylmercapto) which replaced halogen in 2-chlor-4.6-bis-(alkylamino)-simm triazines were more effective as pre-sprout or post-sprout herbicides.

Whorter and Holstum [5] established the fact that for corn, chlorine derivatives of triazine were highly selective and metoxy derivatives were less selective, and methylmercapto derivatives were toxic for weeds and corn as well.

Later Whorter [6], studying the effects of various triazine derivatives on soybeans and weeds, showed that chlorine derivative compounds (excluding trietazine) in this case showed little selectivity. Metoxy and methylmercapto substitutes of triazine which contain an ethylamino radical are more selective for soybeans than are the same substitutes but with an isopropylamino radical.

Our research was undertaken for the purpose of getting quantitative indicators for a comparative evaluation of the biological activity of the more promising triazine derivatives and for studying the occurrence of toxic effects of various crops.

A change in the chemical structure of preparations leads to the occurrence of new phytotoxic properties and a change in herbicidal activity and selectivity. At the same time there is a change in the solubility and absorption of the soil particles which to a considerable degree determine the activity of compounds in the soil [3, 7, 8]. In a solution the action of these factors is limited and there is greater opportunity to determine comparative phytotoxicity. Therefore, we used the method of water cultures.

The plants were grown in glass crystallizers (capacity 400 and 1,200 milliliters), wrapped with thick, colored paper. The tops of the vessels were covered with paraffinized gauze lids with holes for the roots. A 0.5 normal solution of the nutrient mixture of Khoglend and Snayder was used [9]. Prior to planting previously sprouted seeds in the nutrient mixture, there was introduced a dose determined from a chart of a herbicide expressed in milligrams of active substance per liter of nutrient solution. The doses of the herbicides for the variants decreased logarithmically and this made it possible to introduce them by means of progressive dilution of the suspension. The nutrient solutions were scavenged a day later and, depending on the degree of evaporation, distilled water was added. The sample was collected when the damage to the plants from the action of the herbicide was clearly visible for the variant (usually in 15 -- 20 days after setting the sprouts in the vessels). The test was conducted without repetitions but using a great number of doses (9-11) which gave more reliable results for constructing nomograms as described by Starosel'skiy [10].

The nomograms were used to determine $ED_{50}$ -- the value of concentration of the herbicide causing a lowering of the moist weight of the mass above ground by 50% in comparison with a control plant. This indicator was used as a quantitative characteristic of the toxic effect of the herbicide. For example, if the $ED_{50}$ of atrazine for corn is equal to 111.3 milligrams per liter and for oats 0.15 milligrams per liter, it is clear that its toxic effect on oats is much stronger; and in order to achieve the same effect in causing damage it is necessary in the vessels with corn to introduce 740 times more of the herbicide than in the vessels with the oats. During the vegetative period visual observations were made of the condition of the plants for the purpose of finding initial indications of toxicosis.

The research was performed in the summer of 1964 in the vegetation hut of the Ramenskiy Test Field of NIUIF. Sheets [11] informs us that the action of triazine derivatives depends on surrounding conditions. Therefore, in order to avoid the effects of differences in light, temperature, and so forth, on the occurrence of toxic effects, we usually set up the test using one crop but using all preparations simultaneously. Several repetitions of the test using various crops showed that difference in toxicity of crops were incomparably greater than the effects of changes in surrounding conditions.

The items used for the research were Dippe oats, Litovskiye broad beans, Nemchinovskiye peas, and Bukovinskaya 3 corn.

The following herbicides were used:

a) chlorine derivatives of triazine
simazine-2-chlor-4.6-bis-(ethylamino)-simm-triazine,

atrazine-2-chlor-4-ethylamino-6-isopropylamino-simm-triazine,

propazin-2-chlor-4.6-bis-(isopropylamino)-simm-triazine,

ipazin-2-chlor-4-isopropylamino-6-diethylamino-simm-triazine,

trietazin-2-chlor-4-ethylamino-6-diethylamino-simm-triazine, and

khlorazin-2-chlor-4.6-bis-(diethylamino)-simm-triazine

b) metoxy derivatives of triazine

atraton-2-metoxy-4-ethylamino-6-isopropylamino-simm-triazine,

c) methymercapto derivatives of triazine

prometrin-2-methyltio-4.6-bis-(isopropylamino)-simm-triazine.

In Table 1 there are given the values of $ED_{50}$ for the herbicides named when they were introduced into the root area for corn, oats, peas, and beans. Generally the most resistant to triazines was corn and to a lesser extent peas; the most sensitive to trizines were beans and especially oats. However, the effect of triazine derivatives on plants changes greatly with a change in their chemical structure. For example, corn is more sensitive to khlorazin than are beans and peas.

Table 1

$ED_{50}$ of triazine Derivatives for Various Crops (in mg/l of solution)

| Herbicide | Corn | Oats | Peas | Beans |
|---|---|---|---|---|
| Simazine | > 133 | 0,14 | 2,3 | 0,87 |
| Atrazine | 111,3 | 0,15 | 3,0 | 0,65 |
| Propazine | > 133 | 0,18 | 3,9 | 1,2 |
| Triethazine | 46,2 | 1,60 | 6,40 | 11,54 |
| Ipazine | 55,2 | 3,1 | 12,7 | 8,6 |
| Chlorazine | 25,9 | 7,80 | 130,0 | 159,4 |
| Prometrin | 4,4 | 0,70 | 3,8 | 2,2 |
| Atraton | 6,0 | 0,33 | 4,0 | 1,7 |

According to degree of increase of toxic effect on corn, the herbicides[1] which were tested can be aligned in the following order: propazin, simazine, atrazine, ipazin, trietazine, khlorazin, atraton, and prometrin.

With uptake through the roots chlorine derivatives of triazine prove to be less toxic for corn than metoxy and methylmercapto derivatives (atraton and prometrin). 2-Chlor-4.6-bis-(alkylamino)-simm-triazines

1 As will be demonstrated below propazin is considered to be less toxic for corn than simazine because it, in distinction from the latter, did not inhibit thegrowth of the root system.

(simazine and propazin) are far less toxic for corn than 2-chlor-4.6 -bis-(dialkylamino)-simm-triazine (chlorazin).

Among the mixed chlorine derivatives of triazine containing various hydrocarbon radicals in the presence of atoms of nitrogen (atrazine, ipazin, trietazin), the least toxic for corn was atrazine. It should be noted that the most selective for corn propazin, simazine, and atrazine -- were characterized by the presence of undisplaced hydrogen of the amino group. It is possible that this in some way affects the high resistance in corn. With replacement of free hydrogen of the amino groups for a hydrocarbon radical the stability of corn drops considerably. Thus, $ED_{50}$ of atrazine is 111.3 ipazin -- 55.2, and trietazin -- 46.2 milligrams per liter. Khlorazin ($ED_{50}$ -- 25.9 milligrams per liter) is more toxic for corn than are other chlorine derivatives. In khlorazin all atoms of hydrogen of the amino radicals replace the ethyl radical.

If chlorine derivative compounds of triazine are distinguished only by the fact that in one of them the hydrogen of an amino radical replaces an ethyl radical and in another a isopropyl radical, then the second compound usually is less toxic for corn. Propazin is less toxic than simazine and ipazin is less toxic than trietazin.

For oats, peas, and beans the most toxic were simazine, atrazine, and propazin and this is different than in the case of corn. Prometrin and atraton will respect to toxicity for these crops occupy an intermediate position; the least toxic were trietazin, ipazin, and especially chlorazin (Table 1). It follows that for oats, peas, and beans, those of the chlorine derivatives of triazine which are the most toxic are those to which corn demonstrates the greatest resistance and conversely.

Usually it is considered that derivatives of triazine inhibit photosynthesis, acting on the photolysis of water [3, 12, 13]. The first indicators of the effects of these herbicides appear in 10 -- 14 days after sprouting of the seeds and are made manifest by yellowing and withering at the ends of the leaves and then throughout the entire plant [3]. However, observations made by us showed that the indicators of the toxic effect of derivatives of triazine are not the same and depend on chemical structure as well as on the type of plant.

Corn did not show visible signs of toxicosis when simazine and propazin were introduced in a dose of 133.3 milligrams per liter; when this was done there was always considerable sediment on the bottom of the vessels in which the roots grew. Many authors note that corn is able to withstand rather high doses of simazine [14, 15]. Treatment with simazine changes the metabolism of the plants [15, 16]. It causes an increase in the content of nitrogen, potassium, phosphorous, and other elements, and therefore the treated corn can remain green longer in the fall and keep its foliage longer. The supposition has been expressed [15] that roots of corn treated with simazine are able to increase the assimilation of nutrient substances. In connection with this it is interesting to note that in several tests where the plants were not gathered for a long time and the nutrient solution did not change, corn of the control vessels began to yellow and wither while in the vessels treated with simazine it remained dark green.

Simazine and propazine had practically no effect on theweight of the corn mass above ground but simazine, different from propazin, in-

hibits the growth of the roots. (Table 2). The specific weight of the roots of the corn treated with propazin was equal to the specific weight of the roots of the control plants and for the roots treated with simazine even in small doses it was almost half as much. In published literature [15] it has often been remarked that simazine inhibits the growth of roots more than it does that part of the plant above ground.

Based on what has been said it is understandable that propazin should be less toxic for corn than is simazine. This agrees with the findings of Gast [17].

Atrazine caused a decrease in the weight of that part of the plants above ground and also the roots. The growth of the main roots ceased and the formation of short, thickened side roots was observed. That part of the plants above ground was strongly suppressed in growth but the coloring of the leaves remained dark green. The same thing is reported by Hamilton about simazine [18]. Even 70% suppression of corn by simazine was not accompanied by acute toxicosis.

Ipazin, trietazin, and chlorazin lowered the weight of that part of the plants above ground and especially the roots: the specific weight of the roots treated with larger doses of herbicides came to only 3.5 and 10% (Table 3).

Table 2

Moist Weight of the Part Above Ground and the Roots of Corn (in Grams)

| Dose of the Herbicide in Milligrams per Liter | Simazine | | | Atrazine | | | Propazin | | |
|---|---|---|---|---|---|---|---|---|---|
| | Part above Ground | Roots | Specific Weight of Roots, % | Part above Ground | Roots | Specific Weight of Roots, % | Part above Ground | Roots | Specific Weight of Roots% |
| 0 | 10,4 | 6,7 | 40 | 10,4 | 6,7 | 40 | 10,4 | 6,7 | 40 |
| 133,3 | 8,0 | 2,3 | 22 | 6,4 | 1,7 | 21 | 8,1 | 5,6 | 39 |
| 80,0 | 10,4 | 2,5 | 20 | 6,0 | 2,0 | 24 | 10,0 | 6,8 | 40 |
| 48,0 | 10,4 | 2,5 | 20 | 6,7 | 2,3 | 26 | 10,8 | 7,0 | 39 |
| 28,8 | 9,7 | 2,0 | 17 | 8,0 | 3,7 | 31 | 9,3 | 5,9 | 39 |
| 17,3 | 10,4 | 3,1 | 23 | 7,7 | 3,6 | 32 | 9,5 | 6,0 | 39 |
| 8,4 | 10,8 | 3,7 | 26 | 9,5 | 3,7 | 28 | - | - | - |

Table 3

Moist Weight of the Part Above Ground and the Roots of Corn
(in Grams)

| Dose of the Herbicide in Milligrams per Liter | Ipazin | | | Trietazin | | | Khlorazin | | |
|---|---|---|---|---|---|---|---|---|---|
| | Part above Ground | Roots | Specific Weight of Roots % | Part above Ground | Roots | Specific Weight of Roots % | Part above Ground. | Roots | Specific Weight of Roots % |
| 0 | 21.7 | 11,1 | 34 | 21,7 | 11,1 | 34 | 21,7 | 11,1 | 34 |
| 100,0 | 4,9 | 0,2 | 3 | 9,3 | 0,5 | 5 | 8,5 | 0,9 | 10 |
| 60,0 | 8,0 | 0,7 | 8 | 10,6 | 0,8 | 6 | 9,1 | 0,9 | 9 |
| 36,0 | 15,7 | 3,5 | 18 | 12,0 | 0,7 | 6 | 8,7 | 0,9 | 9 |
| 21,6 | 20,7 | 6,5 | 27 | 14,4 | 3,0 | 17 | 10,8 | 1,0 | 9 |
| 13,0 | 23,6 | 10,6 | 31 | 19,2 | 3,1 | 14 | 15,5 | 3,8 | 20 |
| 7,8 | 22,6 | 13,1 | 37 | 20,6 | 2,4 | 10 | 20,3 | 10,0 | 32 |
| 4,7 | 22,0 | 8,3 | 27 | 21,0 | 4,6 | 18 | 20,2 | 9,9 | 32 |

The growth of the part of the corn plants above ground treated with these herbicides was suppressed but the visible signs of toxicosis characteristic for triazine derivatives were not observed (lightening of the leaves, appearance of necrotic spots, withering). Leaves retained their turgor and usual coloring.

The replacement in propazine of chlorine for a methylmercapto radical led to an increase in the toxic effect on corn. The $ED_{50}$ of prometrin (4.4 milligrams per liter) for corn was less than all tested compounds (Table 1). The toxic effect of prometrin was demonstrated in lightening of the middle part of leaves beginning from the base and subsequent spreading along the ribs of the leaves while at the same time theedges of the leaves retained their dark green coloring. The appearance of signs of damage was observed in the bottom, older leaves.

Atrazine suppresses the growth of corn without causing chlorosis; atraton is different in that chlorine replaces the metoxy-radical and acts on the corn altogether differently. Treated plants develop well for 10 -- 15 days and form broader leaves than in the control plants but the color of the entire plant above ground is characterized by an even, lighter (yellowish-green) coloring. As a result the lightening of the leaves increases. Dead parts appear and the plants wither.

The toxic effect of all triazine derivatives (except prometrin and khlorazin) on oats, peas, and beans, appeared in 8 -- 12 days and were expressed in a yellowing of the ends of the leaves while at the same time thecenter remained dark green. Usually chlorosis began with the lower, older leaves. This is connected, as Davis, Funderburk, and Sanging showed [19], with accumulation of simazine at the edges of the leaves and its inability to move to the young leaves. They did not have any noticeable effect on the development of the root system.

The toxic effect of prometrin on oats, peas, and beans, as for corn, is characterized by yellowing of the middle part of the leaves and

a spreading along the ribs while at the same time the ends of the leaves remain dark green. The leaves begin to dry from the inner parts and most often along the ribs there appear dead areas which then spread to the entire leaf. This, probably, is caused by peculiarities of the uptake and accumulation of prometrin in the plants -- peculiarities which are conditioned by the existence of a methylmercapto radical. The root system in plants treated with prometrin developed normally.

Khlorazin, different from all other triazine derivatives which we studied, did not cause the characteristic signs of damage by triazine not only in corn but in oats, peas, and beans. Its toxic effect on oats appears in the retardation of the growth of that part of the plants above ground in which process the coloring of the leaves remains dark green. The growth of theroots decreases and there are formed short, thickened side rootlets (similar to those which are formed in corn due to the effects of atrazine, ipazin, and khlorazin). The toxic effect of khlorazin on peas and beans becomes manifest in the retardation of the growth of that part of the plants above ground while the coloring of the leaves remains dark green. There was observed no visible effect of khlorazin on the growth of the root system of peas and beans.

The described characteristics and the occurrence of toxicosis for plants under the influence of triazine derivatives leads us to think that there is a different mechanism for causing damage to the normal activity of plants. It is difficult to imagine that the destruction of corn due to the effects of atrazine, ipazin, khlorazin, and beans and peas due to the effects of simazine could be a result of disruption of the same processes of metabolism (for example, photosynthesis). It is interesting to note that compounds to which crops prove to be especially resistant (for example, chlorine derivatives for corn and chlorazine for oats, peas, and beans) do not cause chlorosis which is characteristic for toxicosis of triazine and leads only to a stopping of the growth in that part of the plant above ground and disruption of the activity of the root system. The symptoms of damage to plants in this case remind one of the action of herbicides of derivatives of carbamic acid.

In looking over the data which we have obtained it is necessary to keep in mind that under field conditions with different soils and crops and under different test conditions the activity of the compounds named above can be somewhat different. Nevertheless, they are important for a relative comparison of the toxicity of preparations and for an understanding of the physiological-biochemical aspects of their action.

## CONCLUSIONS

1. The values of $ED_{50}$ were obtained for eight of the most promising derivatives of triazine for corn, oats, peas, and beans.

2. According to degree of increase of toxic effect on corn, the tested preparations are arranged in the following order: propazin, simazine, atrazine, ipazin, trietazin, khlorazin, atraton, and prometrin.

3. For peas, beans, and oats the most toxic are simazine, atrazine, and propazin; prometrin and atraton occupy intermediate places and ipazin and trietazin and especially khlorazin are the least toxic.

4. The first signs of the toxic effect of triazine derivatives are not always the same and are determined by the chemical structure of

the herbicide as well as by the peculiarities of the crop in question.

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